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Experiments have demonstrated the feasibility of solid state lasers based on vibrational transitions, and point toward the possibility of new high power and tunable sources in the infrared. The great importance of V-V transfer processes in this solid state context, however, has shown that further advances will strongly depend on the understanding of the vibrational energy transfer phenomena.

Other research led to the development of a new solid state high resolution spectroscopic technique which was used to investigate dynamical properties of the KI:NO_2^- system.

This research resulted in the first demonstration that persistent IR spectral holes can be used to identify the isotope shifts of the FIR gap modes associated with NO_2^- in KI. By studying the isotope dependence it was determined that two of the modes are translational while the third has a mixed translational-librational character. It is the findings for this third mode which are most interesting since the properties

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of the mixed mode disagree in a fundamental way with the predictions of the previous lattice dynamical calculation for this defect-lattice system.

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Army Research Office Graduate Fellowships

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Two Ph.D. students were supported throughout their graduate career under the ARO fellowship program. Their research accomplishments are outlined below.

T. R. Gosnell made the first observation of infrared laser oscillation from a purely vibrational transition in the solid state. The laser-active medium consisted of CN^- molecular ions substitutionally doped into KBr, KI, and RbI alkali halide host lattices, and oscillation was observed on the 2->1 and 3-> 2 vibrational transitions of CN^- at $\lambda = 4.9$ μm when the samples were cooled to 1.7 K. Population inversions in these systems were directly produced by optical pumping of the upper laser level using a KCl:Li$(F_2^+)_A$ color-center laser, which was tunable to the weakly-allowed 0 -> 2 first overtone transition of CN^-, and a NaCl:K$(F_2^+)_A$ color-center laser which was tunable to the very weak 0 -> 3 second overtone. In addition, a unique indirect pumping mechanism was discovered: Through coupling of their dynamic electric dipole momemts, pairs of CN^- ions excited to the v = 1 state by a 100-nsec 4.8μm pulse from a frequency doubled CO_2 TEA laser undergo an exchange vibrational energy (V-V transfer), yielding for each donor/acceptor pair one ground state ion and a doubly-excited ion. This cross relaxation process was sufficiently rapid, compared with the vibrational relaxation rate for an isolated ion (20-40 sec^{-1}), that a population inversion readily evolves between the v = 2 and v = 1 levels, which lead to pulsed lasing on the 2 -> 1 vibrational transition.

A second important consequence of V-V transfer was the observation of CW lasing on the 2 -> 1 transition from samples pumped continuously on the 0 -> 1 transition. Ordinarily, the long lived v = 1 level would provide a vibrational energy bottleneck preventing continuous oscillation, but the reduction of the effective vibrational lifetime of the v = 1 level resulting from intermolecular energy transfer removes this bottleneck, and CW lasing was obtained.

These experiments have demonstrated the feasibility of solid state lasers based on vibrational transitions, and point toward the possibility of new high power and tunable sources in the infrared. The great importance of V-V transfer processes in this solid state context, however, has shown that further advances will strongly depend on the understanding of the vibrational energy transfer phenomena.

The thesis research of P.W. Ambrose led to the development of a new solid state high resolution spectroscopic technique which he applied to investigate dynamical properties of the KI: NO_2^- system. Initially, tunable infrared diode lasers are used to burn persistent IR spectral holes (PIRSHs) in the internal vibrational spectrum of NO_2^- defects in KI at low temperatures through a reorientational form of hole burning. Next, the technique of PIRSH burning in the internal bending mode of NO_2^- is combined together with high resolution FIR fourier transform interferometry to probe simultaneously the NO_2^- gap features. Persistent polarized changes in the FIR spectrum are coupled to persistent changes in the internal vibrational mode spectrum but the production of persistent holes in the IR does not translate into FIR holes in the external modes. The results show that the three FIR absorption lines in the gap are consistent with localized translational motion of the NO_2^- ion.

His next discovery was that persistent IR hole burning could be used to identify the orientation of the molecule in its ground state. Irradiation of an internal vibrational mode of KI:NO_2^- at low temperatures with a low intensity tunable IR diode laser produces a PIRSH in the inhomogeneously broadened absorption band through a reorientational form of hole burning. Since the IR bending vibration transition moment is parallel to the permanent dipole moment of the symmetric molecule, burning this mode reorients only those NO_2^- ions which have nonzero permanent dipole projections along the burn laser polarization. Hence, probing the hole depth as a function of burn

and probe laser polarization uncovers the original burned dipole orientation.

In addition to showing that three FIR gap modes with comparable strengths occur for NO_2^- in KI, not two as previously determined and establishing the ground state orientation of the molecule, he also demonstrated that the Raman active mode is still not coincident with any of these transitions. Since three FIR/Raman active gap modes are allowed for a C_{2v} molecule, the origin of the entire FIR spectrum is once again open to question. The possibility that this spectrum is mainly translational or librational in character or even that the Raman and FIR results obey the parity selection rule just as for a point defect in a cubic lattice was still unresolved.

To solve this riddle he made the first identification of the isotope effect on the FIR gap mode spectrum by PIRSH burning and establish it as the technique par excellence for assigning spectral lines to a particular isotopic species of NO_2^-. The substitution of ^{18}O for ^{16}O and ^{15}N for ^{14}N in NO_2^- produces gap mode frequency shifts for two of the three modes consistent with translational mode behavior. The ^{15}N for ^{14}N substitution also demonstrates that the intermediate mode for the most abundant isotopic species does have some librational character even though it does not appear in the Raman spectrum. This new level of FIR sensitivity confirms that the two spectroscopic techniques do probe orthogonal aspects of the defect dynamics.

His work is the first demonstration that persistent IR spectral holes can be used to identify the isotope shifts of the FIR gap modes associated with NO_2^- in KI. By studying the isotope dependence he determined that two of the modes are translational while the third has a mixed translational-librational character. It is the findings for this third mode which are most interesting since the properties of the mixed mode disagree in a fundamental way with the predictions of the previous lattice dynamical calculation for this defect-lattice system.

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